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Humic acid removal efficiency from aqueous solutions using graphene and graphene oxide nanoparticles

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ABSTRACT

Humic acid materials (humic acid and fulvic acid) form the most important section of natural organic materials in water resources. These materials cause a lot of secondary problems, when drinking water is under treatment. Many different methods have been considered for removal of humic acid from aqueous solution. Adsorption process is a common method for removal of humic acid that seems attractive for many experts. The aim of present study is to examine and compare the adsorption of humic acid by graphene and graphene oxide nanoparticles. This experimental research has been done in a bath condition. The effects of various parameters such as pH, contact time, initial concentration of humic acid, adsorbent dosage, and temperature on the removal of humic acid by graphene (G) and graphene oxide (GO) adsorbents have been examined. The maximum amount of humic acid removal by these adsorbents occurred when pH = 3 and initial concentration = 10 mg/L. Also, the adsorption capacity for graphene and graphene oxide in removal of humic acid in optimum experimental conditions were 41.4 and 39.3 mg/g, respectively. The results of adsorption isotherms showed that adsorption of humic acid by G and GO adsorbents follows the Freundlich and Langmuir model, respectively. The results show that the pseudo-second-order kinetic model correlates well with experimental data. The results of examining the thermodynamics of reaction showed that the removal of humic acid is an exothermic reaction.

Keywords: Adsorption; Humic acid; Graphene; Graphene oxide

1. Introduction

Humic acid materials (humic acid and fulvic acid) form the most important section of natural organic materials in water resources that consists of the decomposition of animal and plant material breakdown [1,2]. The structure of humic acid includes a chain of alkyl groups and aromatic units with reactive carboxylic groups, hydroxyl and quoin groups [3]. Fig. 1 shows the chemical structure of humic acid.

In water treatment, humic acid react with chlorine antiseptics in water environments and produces disinfection by products (DBPs), and it has been confirmed that these byproducts can cause cancer [5]. These materials cause a lot of secondary problems, when drinking water is under treatment, some of these problems including unpleasant effects on color and taste, increasing the presence of heavy metals and poisonous materials, decreasing the effects of water treatment methods such as coagulation and adsorption processes, negative effects on operation of membranes, increasing of the microorganisms growth in water supplies and water distribution networks and also increasing the consumption of disinfectant materials [6,7]. Therefore, it is very important to identify and remove these materials from water sources.

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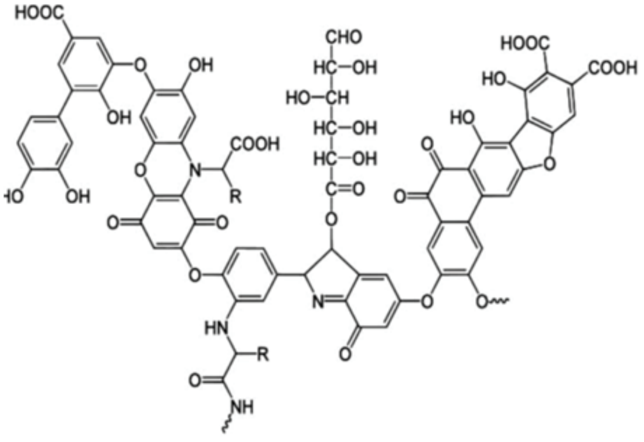


Fig 1. Chemical structure of humic acid [4].

Various methods including, electrocoagulation [8], photocatalysis [9], filtration [10], advanced oxidation [11], adsorption [12] and etc for removal of humic acid have been used. Among these methods, adsorption has been widely used because of its simple, effective, low cost, flexibility and simplicity of design and easy operation [13,14].

Many adsorbents such as activated carbon [15], bentonite [16], zeolite [17] and chitosan [18] for the removal of humic acids from water have been developed. Suitable adsorbents should have features such as strong adsorption of pollutants, large surface area, and high pore volume with more binding sites [19]. Also, Specific surface area and small size of adsorbent particles are two important factors that determine the efficiency of adsorption process. Therefore in recent years, nano adsorbents (such as nano carbons, carbon nanotubes, carbon nanotubes, nano oxides and etc), have been widely used in order to removal of environmental pollutants [20–22]. Various types of efficient, low-cost and environmentally friendly nanomaterials for use in detoxification of industrial wastewater, groundwater, surface water and drinking water have been reported [23]. Meanwhile, graphene and graphene oxide nanomaterials are adsorbents that have been investigated for application in waste water treatment [23,24].

Graphene, a two-dimensional (2D) honeycomb material with a C-C bond length of 0.142 nm, has been identified and analyzed in recent years [25]. Nano graphene as a new appearing has special physical, chemical, electrical and mechanical properties [26]. Also, it has a huge specific surface area (theoretical value 2630 m^2/g). Graphene has special physical properties. Finding the room-temperature quantum hall effect [27], fast electron mobility, high charge carrier density [28], high thermal conductivity, flexibility [29], large accessible surface area and excellent mechanical strength [30] are important features of graphene.

Because high quality sheets of graphene is often prepared by chemical vapor deposition [31], which requires expensive equipment, many groups have looked at using graphene oxide as a solution process able alternative for the preparation of graphene like materials [32]. Also, graphene is generally considered to be non-polar and hydrophobic. In return, Graphene oxide (GO), contains much more polar moieties, such as hydroxy, epoxy, and carboxy groups, and so has a more polar and hydrophilic character than graphene [33]. Graphene oxide has a single layer of carbon structure that features such as high surface area, density and crystalline state has a honeycomb lattice. The presence of epoxide, carboxyl and hydroxyl groups in the surface of graphene oxide and the high surface area of this compound have caused much attention to this adsorbent to remove various pollutants in water and waste water [34].

Due to the numerous advantages of this method, so it has been attracted many experts. Omri et al. performed a study in 2013 entitled removal of humic acid by activated carbon synthesized from almond shell as a method for purification of industrial solution of phosphoric acid. The results of their study showed activated carbon prepared from almond shell seems to be an effective, low-cost, and good adsorbent precursor for the removal of humic acid from commercial phosphoric acid solution [35]. Hartono et al. performed a study in 2009 entitled removal of humic acid from aqueous solution by graphite oxide nanoparticles. The results of their study showed that when the pH increases, then the efficiency of adsorption decreases, and when the adsorbent dosage increases, then the amount of adsorption increases as well [21]. Yang et al. conducted a research entitled "Graphene oxide-iron oxide and reduced graphemeoxide-iron oxide hybrid materials for the removal of organic and inorganic pollutants ", in which it was found that the RGO-iron oxide material was a good adsorbent for 1-naphthol and 1-naphthylamine but not for Pb(II), whereas the GO-iron oxide material was a good adsorbent for Pb(II) but not for 1-naphthol and 1-naphthylamine due to oxygen-containing groups on the surface [36].

The aim of this study was to examine the effectiveness of graphene (G) and graphene oxide (GO) adsorbents for removal of humic acid from aqueous solution. We also examined the thermodynamics, isotherms and kinetics of the process.

2. Materials and method

2.1. Materials

In this study, the effectiveness of G and GO adsorbents for removal of humic acid from aqueous solution at laboratory scale was investigated. Iranian nanotechnology research center of petroleum industry provided the G and GO adsorbents for this research. The required chemical materials of this study such as HCl, NaOH were purchased from MERK Company productions. The humic acid with purity of 55% was prepared from Acros Company. UV-visible spectrophotometer (UV/VIS spectrophotometer T80, PG Instrument Ltd) was used for detect the humic acid at 254 nm wavelength. pH meter (pH-meter Knick, 765 Caliamatic) was used to determine the pH . Shaker incubator (COMBI- SHAKER, Model NB-101MT) was used to mix the samples.

2.2. Adsorption experiments

A specific amount of humic acid powder was added to one liter of deionized water in order to prepare humic acid stock solution of 400 mg/L. Then this solution was diluted in order to have solutions with initial humic acid concentrations of 2, 5 and 10 mg/L. Various parameters such as pH (3, 5, 7, 9 and 11), initial concentration of humic acid (2, 5 and 10 mg/L), contact times (5, 10, 15, 30 and 45 min), adsorbent dosage (0.1, 0.2, 0.3 and 0.4 g/L) and temperature (15, 25 and 35°C) for both adsorbents were separately examined and the results were compared with each other at the end of the experiments. In order to examine the effects of each parameter, the specific parameter were changed in all levels of the experiment and other parameters were kept fixed.

Finally, adsorption capacity of humic acid was calculated by Eq. (1):

$$q_e = \frac{C_o - C_e}{m} V \tag{1}$$

where C_0: Initial concentration of humic acid in the solution (mg/L), C_e: Final concentration of humic acid after contact time (mg/L), q: Adsorption capacity (mg/g), V: Volume of solution (ml) and m: Adsorbent dosage (g) [37].

2.1.1. *pH effect on adsorption*

The pH effect on the process of adsorption humic acid onto G and GO was performed by changing the pH of the humic acid solution in the range of 3–11. Solutions of NaOH and HCl (1 and 0.1 N) were used for adjusting and modifing the various pH values. Then, the effect of pH was investigated by using of 0.01 g of G and GO in 100 mL of humic acid solution (10 mg /L). The solutions were put on the shaker for 60 min with 240 rpm. Finally these solutions passed through 0.2 micrometer filters and measured by spectrophotometer at wavelength of 254 nm.

2.1.2. *Effect of initial concentration of humic acid and contact time on adsorption*

At this stage, time and initial concentration of humic acid were changing but all other parameters were kept fixed. The adsorption amount of humic acid was examined with different concentrations (2, 5 and 10 mg/L) at different contact times (5, 10, 15, 30 and 45 min) while the pH value and optimal amounts of adsorbent were determined in previous stages. Then the sample passed through the 0.2 micrometer filters and finally the sample was measured by spectrophotometer at wavelength of 254 nm.

2.1.3. *Effect of adsorbent dosage on adsorption*

At this stage, the effect of adsorbent dosage (0.1, 0.2, 0.3 and 0.4 g/L) by maintaining the optimum conditions obtained from the previous steps on the removal of humic acid was investigated. Finally, as in the previous steps, after passing the sample from the 0.2 micrometer filter, the concentration of humic acid was measured by spectrophotometer.

2.1.4. *Adsorption thermodynamics*

In order to examine the effects of temperature on humic acid removal efficiency, humic acid solution with initial concentration of 10 mg/L were prepared. In this stage, the pH and adsorbent dosage was adjusted to the optimal values that determined in the previous stages. Then this solution was shaken and mixed inside shaker incubator for 60 min at different temperatures (15, 25 and 35°C).

In the study of thermodynamics, determination of parameters such as enthalpy change (ΔH), entropy change (ΔS) and Gibbs free energy change (ΔG) is essential. To determine these parameters, the following equations were used:

$$k_d = \frac{q_e}{C_e} \tag{2}$$

$$\Delta G° = -RT \ln k_d \tag{3}$$

$$\ln k_d = -\frac{\Delta H°}{RT} + \frac{\Delta S°}{R} \tag{4}$$

where K_d is the thermodynamics equilibrium, ΔG° is Gibb's free energy, ΔS° is entropy, ΔH° is enthalpy, R is the universal constant of the gasses (8.314 J/mol·K), T is the absolute temperature [38].

2.1.5. *Adsorption isotherms*

In this research, the experimental data on adsorption equilibrium with Langmuir and Freundlich isotherms were investigated. The Langmuir and Freundlich isotherms were calculated using the following equations, respectively:

$$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \tag{5}$$

where Q_m is the maximum amounts of humic acid adsorbed (mg/g), K_L is the constant of Langmuir equation and C_e (mg/L) is the concentration of remaining humic acid in equilibrium [39].

$$q_e = K_f C_e^{\frac{1}{n}} \tag{6}$$

where q_e (mg/g) is the amount of humic acid adsorbed of the adsorbent at equilibrium, C_e (mg/L) is the equilibrium concentration of adsorbate and K_f is Freundlich isotherm constant [39].

2.1.6. *Adsorption kinetics*

The adsorption kinetics was studied with pseudo first and pseudo second order kinetic models that generally presented in the following equations, respectively:

$$\frac{dq_t}{dt} = K_1 \left(q_e - q_t\right) \tag{7}$$

$$\frac{dq_t}{dt} = K_2 \left(q_e - q_t\right)^2 \tag{8}$$

where *qe* is the amount of humic acid adsorbed on adsorbent at equilibrium and *q* is amount of humic acid adsorbed on adsorbent at various times (mg/g), k_1 and k_2 are the rate constant of the pseudo first-order model (1/h) and the rate constant of the pseudo second-order model (g/mg·h), respectively [40].

3. Results and discussion

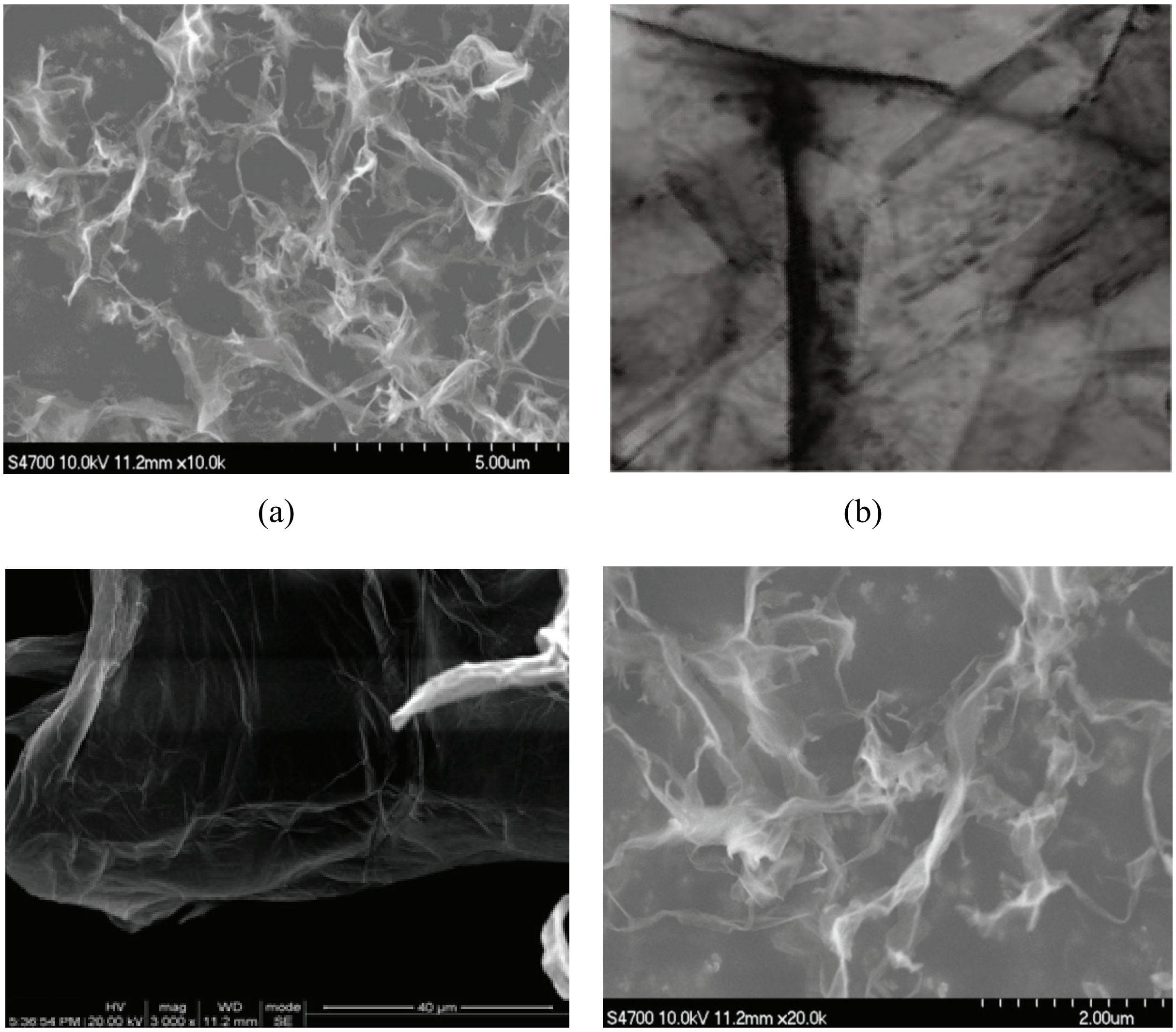
3.1. Characterization of the adsorbents

Fig. 2 show SEM and TEM images for G and GO adsorbents. For determination of the accurate diameter of G and GO adsorbents bundles, the SEM method was used. This technique gives information mainly regarding surface morphology of the G and GO samples. The TEM was used for measurement of G and GO diameter in the bundle [41,42]. From the TEM image it is possible to determine directly the diameter of one nanoparticle and bundle diameter. Using this information the number of G and GO in the bundle can be found. According to Fig. 2 the thickness of the layers of Gused in this study was 2–18 nm. Furthermore the thickness of the layers as well as the number of layers of GO adsorbent was 3.7–4 nm and 6–10, respectively.

3.2. The effects of solution pH on the removal of humic acid

The results of examining the effects of pH values of the solution on the humic acid adsorption by G and GO adsorbents are shown in Fig. 3. Regarding to this figure, with increasing the pH of the solution from 3 to 11, the humic acid removal efficiency decreases. At pH = 3 the adsorption capacities of G and GO were 23.78 and 28.58 mg/g, respectively. Therefore, there is a reverse relationship between the pH values and adsorption capacities.

The results showed that with increasing the pH values, adsorption capacity decreases. In acidy pHs, humic acid has a high solubility and this has effects on its adsorption. Also, pH has effects on the surface density and therefore



(a) (b)

(c) (d)

Fig. 2. (a) SEM and (b) TEM images of G adsorbent (c) SEM and (b) TEM images of GO adsorbent.

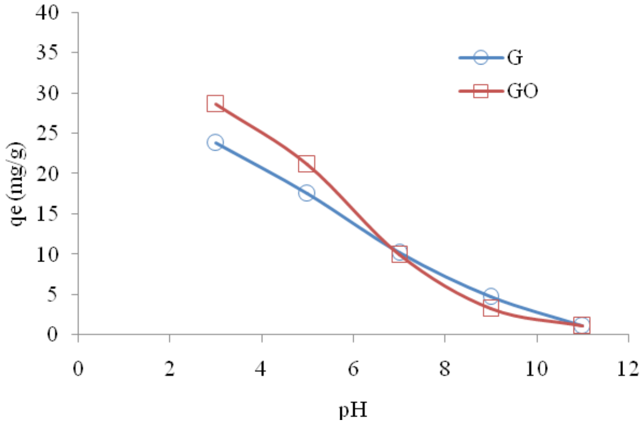


Fig. 3. Effects of pH on removal of humic acid by the G and GO adsorbents (dosage adsorbent = 0.1 g/L, initial concentration of humic acid = 10 mg/L, contact time = 45 min).

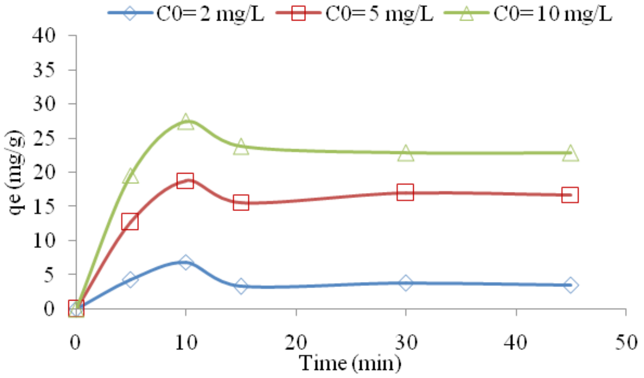


Fig. 4. Effects of reaction time and initial concentration of humic acid on the efficiency of removal process by G adsorbent (pH = 3, adsorbent dosage = 0.1 g/L).

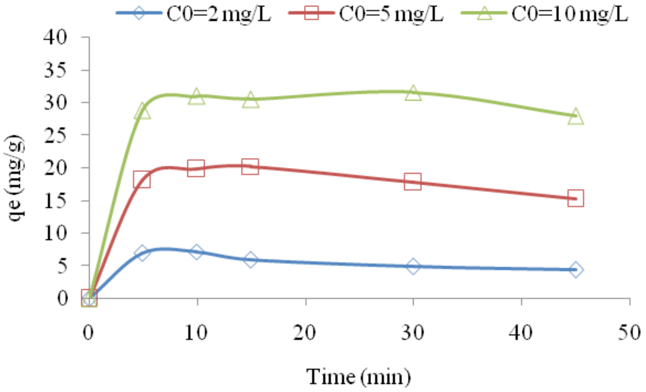


Fig. 5. Effects of reaction time and initial concentration of humic acid on the efficiency of removal process by GO adsorbent (pH = 3, adsorbent dosage = 0.1 g/L).

has effects on the adhesion force between the particles. in the adsorption process, H^+ ad OH^- are two important ions and determining ions for the surface charge [20]. The type of humic acid ion affects on the reaction between the humic acid and adsorbent. In other words if the surface charge of adsorbent is positive, then its tend to adsorb anions increases and electrostatic adsorption takes place. Therefore the pH of the solution affects on both the surface charge of the adsorbent and the humic acid charge and these conditions control the humic acid adsorption. In higher pHs, the surface charge of the adsorbent is negative and so the adsorbent tend to adsorb the anions by the electrostatic process decreases. the adsorption process is dependent to some factors like the number of silanol (Hydoxil groups that exists on the adsorbent surface, composition of solution ions, chemical and physical characteristics of humic acid [43,44]. In addition, it is probable that with increasing the pH, the spherical shape of humic acid molecules becomes linear and this decreases the humic acid adsorption in higher pHs [21]. Similar results were observed in the study of Omriand et al. [35].

3.3. The effects of contact time and initial concentration on the removal of humic acid

Effects of contact time and initial concentration of humic acid on the efficiency of removal of humic acid are shown in Figs. 4 and 5. As shown in these figures, the removal of humic acid by increasing the contact time for up to 10 min has been increased. Also, the results show that at humic acid concentrations of 2, 5 and 10 mg/L in contact time 10 min, the adsorption capacities of G adsorbent were 6.85, 18.78 and 27.48 mg/g, respectively. Also the adsorption capacities of GO adsorbent at mentioned initial humic acid concentration were 7.19, 19.83, 31.01 mg/g, respectively.

According to Figs. 4 and 5, there is a reverse relationship between the contact time and removal of humic acid. Adsorption kinetics is highly dependent on the adsorption surface. In the first minutes, the maximum amount of free surfaces on the adsorbent exists and this is compatible with the results of this study. The results show that the amount of humic acid adsorption is a function of its initial concentration. With increasing the initial concentration of humic acid, the adsorption capacity increases as well the results of experiments in this stage confirm the studies of Wang and et al. Their study was about removal of fulvic acid from aqueous solution by modified zeolite. Their results showed that with increasing the concentration, the removal of fulvic acid by modified zeolite increases as well and when time reaches 120 min, the concentration reaches to equilibrium. The results show that adsorption amount of fulvic acid is a function of its initial concentration. Also, increasing the initial concentration, causes the interaction between adsorbent and fulvic acid to increase [44]. In this study, the maximum amount of adsorption occurred in the first 10 min and for G in higher contact times, adsorption capacities decreased. But for GO, the maximum absorption capacity was 10 min and after that it was almost constant. These changes in higher contact times are probably because that in initial contact times, most sites on the adsorbent surface are empty and concentration changes of the pollutant in liquid phase are higher and with increasing the time, less of these empty sites on the adsorbent surface exist. Therefore the speed of pollutant concentration changes in liquid phase decreases and consequently the speed of adsorption decreases. On the other hand, with increasing the time, the repulsive force between the adsorbed molecules of humic acid on the surface of adsorbent increases and therefore the adsorption in the empty sites of adsorbent surface takes place with a lower speed. This causes the adsorption process to take more time, or in the other words, the amount of adsorption versus the time decreases [44]. Generally, surface adsorption of humic acid on adsorbents such as graphene and graphene oxides is described by mechanisms such as electrostatic interactions, hydrophobic interactions (such as van der Waals forces), π-π reactions, and hydrogen bondings. Due to the graphite structure of graphene and graphene oxides, in many cases its characteristics are similar to those of activated carbon. Adsorption and desorption between hydrophobic humic acid and graphene and graphene oxides due to their surface charge type, van der walls forces in will also occur due to the hydrophobic surfaces of the graphene and graphene oxides. The π-π reactions are also due to the aromatic rings present in humic acid. Hydrogen bonds Because of humic acid may act as hydrogen donors, they are used to describe the adsorption of humic acid on adsorbents such as graphene and graphene oxides. The cause of the effect of hydrogen bonds is the presence of a large number of carboxylic or phenolic groups of humic acid [45]. Lu and Su studied the adsorption of natural organic matters (NOM) by carbon nanotubes. Their results showed that with increasing the initial concentration of NOM and ionic power of solution, the amount of NOM adsorption by carbon nanotubes increased, but with increasing the pH, adsorption decreased [12].

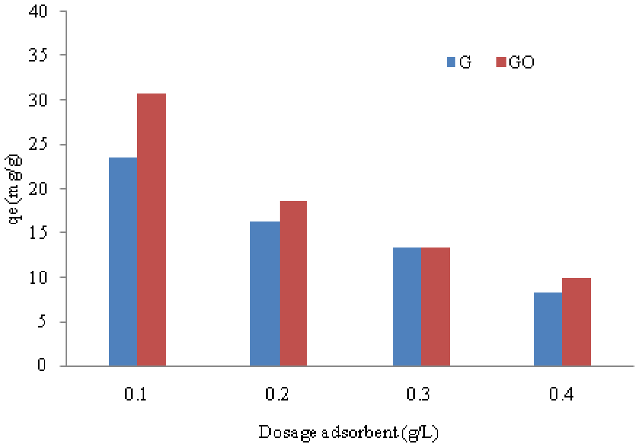


Fig. 6. Effects of various adsorbent dosage on the efficiency of humic acid removal by G and GO adsorbents (pH = 3, initial concentration = 10 mg/L, contact time = 10 min).

3.4. Effects of dosage adsorbent on the removal of humic acid

The results of effects of various dosage of adsorbent G and GO adsorbents (0.1, 0.2, 0.3 and 0.4 g/L) on the removal of humic acid in pH = 3, equilibrium time = 10 min can be seen in Fig. 6. Regarding this figure, the optimal concentration for G and GO adsorbents was calculated to be 0.1 g/L. In this stage, with the optimum amounts of adsorbent, the adsorption capacity of G adsorbent was 23.62 mg/g and this number for GO adsorbent was 30.84 mg/g.

The results of studying the effects of optimum dosage of adsorbent on the humic acid adsorption are in Fig. 6. According to the results, with increasing the adsorbent dosage from 0.1 to 0. 4 g/L, the adsorption capacity of humic acid onto G and GO decreases. This is because of some factors such as active surface area of the adsorbent and some dynamic factors such as an increasing in interactions and free bands on the adsorbent surface. In such conditions, there is a competition between the molecules of the pollutant to fill the empty surfaces of the adsorbent and therefore the adsorbent surfaces are used in an unsaturated manner and so all of adsorbent capacities are not used optimally. Therefore, the amount of pollutant adsorption decreases. These results were confirmed by the results of Moriguchi and et al about application of silica nanoparticles modified with heavy metals for removal of humic acid [20].

3.5. Effects of temperature and thermodynamic studies

The results of examining the effect of reaction temperature on the removal process of humic acid by two mentioned adsorbents are shown in Table 1. It can be seen, increasing the solution temperature decreases the amount of humic acid adsorption by both adsorbents. This shows that the removal process of humic acid by both adsorbents is an exothermic reaction.

With increasing the temperature from 288 to 308 K, the efficiency of G and GO adsorbents for removal of humic acid decreased. Also, the negative amounts of ΔH° show that the process is exothermic and with decreasing the environment temperature, the adsorption capac-

Table1
Thermodynamic parameters for humic acid adsorption on G and GO adsorbents

T(K)	G					GO				
	q (mg/g)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol K)	R^2	*q* (mg/g)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol K)	R^2
288	41.43	–2.49	–21.96	–67.94	0.94	39.31	–2.28	–3.28	–3.46	0.98
298	31.48	–1.51				38.47	–2.27			
308	28.11	–1.15				37.2	–2.21			

ity increases. Also according to Table 1 the negative amounts of ΔG° shows that the removal of humic acid by two mentioned adsorbents can be done in stoichiometry manner and this reaction is done spontaneously. Negative amounts of ΔS° show the humic acid molecules at the solid–liquid interface are more organized than those in the bulk solution phase [4,46,47].

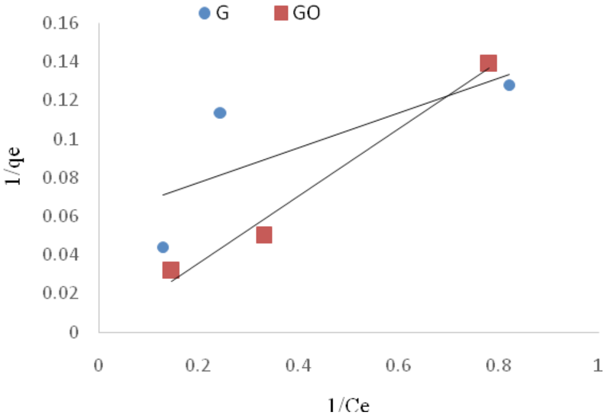


Fig. 7. Langmuir isotherm for removal of humic acid by G and GO adsorbents.

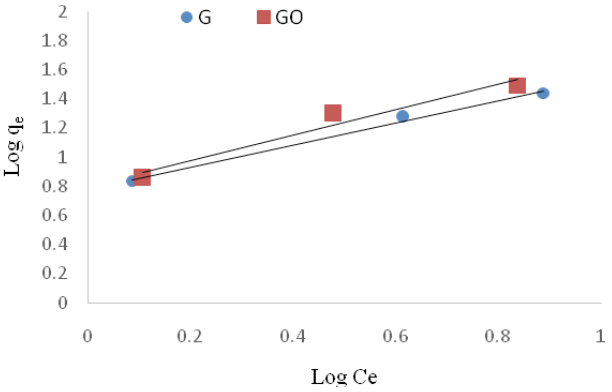


Fig. 8. Freundlich isotherm for removal of humic acid by G and GO adsorbents.

3.6. Adsorption isotherms

The results of Langmuir and Freundlich models for adsorption of humic acid onto G and GO adsorbents are shown in Figs. 7 and 8 and also Table 2.

As shown in Figs. 7 and 8 and Table 2, adsorption of humic acid by G adsorbent with $R^2 = 0.99$ follows the Freundlich model and this shows that the surface of G adsorbent is heterogeneous and the adsorption of humic acid on G occurred layer by layer [24,49]. But adsorption of humic acid on GO adsorbent with $R^2 = 1.00$, followed the Langmuir model and according to this model, the humic acid adsorption was single layer and homogenous [24,49].

3.7. Adsorption kinetics

To investigate the mechanism of humic acid adsorption on G and GO adsorbents, the pseudo-first-order and pseudo-second-order equations were used to find out the adsorption mechanism. The results of kinetic parameters for adsorption of humic acid onto G and GO adsorbents are shown in Table 3.

Regarding Table 3, by comparing the amounts of R^2 for G and GO, it is clear that the adsorption of humic acid for these adsorbents follows the pseudo second order kinetics. On the other hand, with studying the pseudo second order equations, it can be seen that there is little difference between capacity of adsorption under empirical equilibrium conditions (q_{cal}) and the capacity of adsorption under calculation based conditions (q_{exp}). So, pseudo second order kinetic model can be used properly for explaining the kinetics of humic acid with G and GO adsorbents. The findings of Naghizadeh and et al. confirm these results [4].

3.8. Comparison of the G and GO adsorbents with other adsorbents

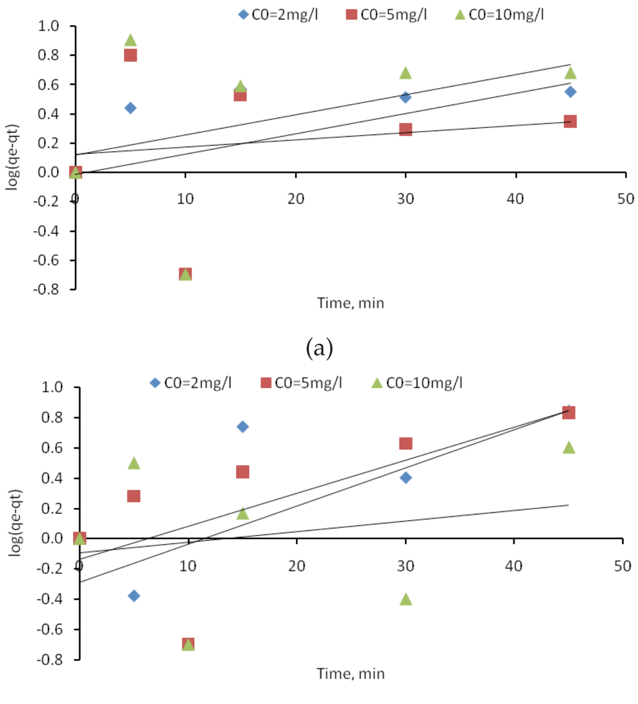
The comparison of the maximum adsorbed capacity in this study is important with other amounts of reported adsorbents. For this reason, the capacity adsorption of humic acid using G and GO adsorbents has been compared with other adsorbents, as shown in Table 4.

Table 3
Comparison of the pseudo-first-order and pseudo-second-order models for different initial humic acid concentrations

Adsorbents	C_0 (mg/L)	Pseudo-first-order			Pseudo-second-order			$q_{e,exp}$ (mg/g)
		K_1 (min^{-1})	$q_{e,cal}$ (mg/g)	R^2	K_2 (g/mg min)	$q_{e,cal}$ (mg/g)	R^2	
G	2	0.03	0.97	0.22	0.20	3.44	0.99	7.05
	5	0.01	1.33	0.03	0.13	17.00	0.99	18.98
	10	0.03	1.32	0.39	0.16	22.83	1.00	27.69
GO	2	0.06	0.51	0.48	0.05	5.76	0.91	12.39
	5	0.05	0.73	0.46	0.03	25.33	0.91	32.03
	10	0.02	0.80	0.43	0.05	45.63	1.00	49.04

Table 4
Comparison of the G and GO adsorbents with other adsorbents

Adsorbent	C_0 (mg/L)	T (K)	q_e (mg/g)	Reference
Graphene	2–10	288	41.4	This study
Graphen oxide	2–10	288	39.3	This study
Carbon prepared from almond shell	10–100	318	169.5	[35]
Magnetic chitosan nanoparticle	3–30	298	32.6	[50]
Walnut shell	10–30	298	35.2	[4]
Walnut shell modified with titanium dioxide	10–30	298	40.2	[4]
Walnut shell modified with zinc oxide	10–30	298	37.9	[4]
Crosslinked chitosan–epichlorohydrin beads	10–50	300	44.8	[51]



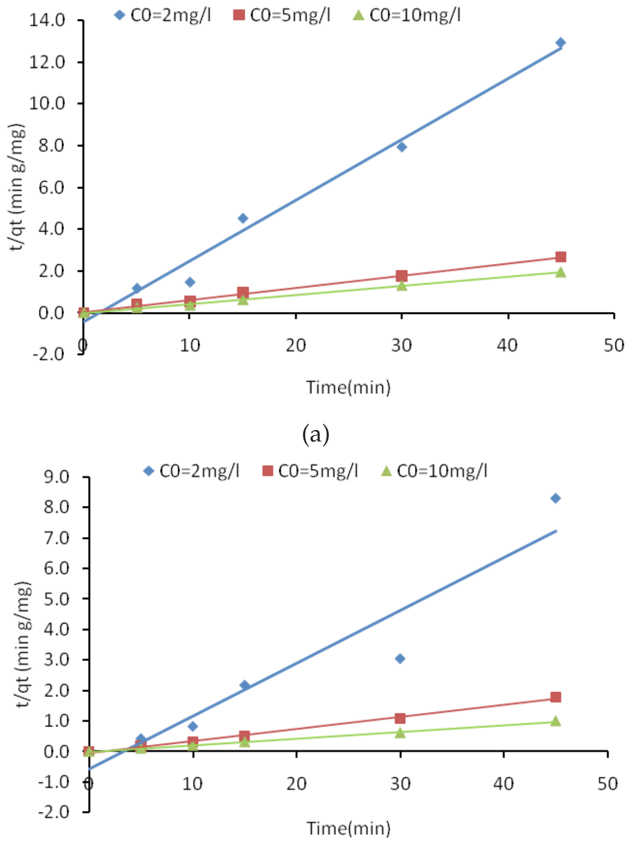
(a)

(b)

Fig. 9. Pseudo-first-order kinetics for adsorption of humic acid onto (a) G and (b) GO adsorbents.

4. Conclusion

In this study, the G and GO adsorbents were used as adsorbents for removal of humic acid from aqueous solution. At pH of 3, the highest amounts of removal were observed. Also it was observed that increasing the initial concentration of humic acid and decreasing the adsorbent dosage caused the adsorption to increase. According to the results, it can be clearly seen that GO adsorbent have a higher efficiency than G adsorbent for removal of humic acid. The results of adsorption isotherms showed that adsorption of humic acid by G and GO adsorbents follows the Freundlich and Langmuir model, respectively. Also, the results show that the pseudo-second-order kinetic model correlates well with experimental data. The thermodynamic studies also showed that the removal of humic acid by G and GO adsorbents was exothermic and spontaneous.



(a)

(b)

Fig. 10. Pseudo-second-order kinetics for adsorption of humic acid onto (a) G and (b) GO adsorbents.

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References

[1] J. Feng, B.-w. Zhu, T.-T. Lim, Reduction of chlorinated methanes with nano-scale Fe particles: Effects of amphiphiles on the dechlorination reaction and two-parameter regression for kinetic prediction, Chemosphere, 73 (2008) 1817–1823.

[2] S. Babel, P.A. Sekartaji, H. Sudrajat, TiO_2 as an effective nanocatalyst for photocatalytic degradation of humic acid in water environment, J. Water Supply Res Technol.-Aqua, 66 (2017) 25–35.

[3] Y. Zhan, Z. Zhu, J. Lin, Y. Qiu, J. Zhao, Removal of humic acid from aqueous solution by cetylpyridinium bromide modified zeolite, J. Environ. Sci., 22 (2010) 1327–1334.

[4] A. Naghizadeh, H. Shahabi, F. Ghasemi, A. Zarei, Synthesis of walnut shell modified with titanium dioxide and zinc oxide nanoparticles for efficient removal of humic acid from aqueous solutions, J. Water Health, 14 (2016) 989–997.

[5] B.R. Eggins, F.L. Palmer, J.A. Byrne, Photocatalytic treatment of humic substances in drinking water, Water Res., 31 (1997) 1223–1226.

[6] C.R. Reiss, J.S. Taylor, C. Robert, Surface water treatment using nanofiltration—pilot testing results and design considerations, Desalination, 125 (1999) 97–112.

[7] Á. de la Rubia, M. Rodríguez, D. Prats, pH, Ionic strength and flow velocity effects on the NOM filtration with TiO_2/ZrO_2 membranes, Sep. Purif. Technol., 52 (2006) 325–331.

[8] E. Bazrafshan, H. Biglari, A.H. Mahvi, Humic acid removal from aqueous environments by electrocoagulation process using iron electrodes, J. Chem., 9 (2012) 2453–2461.

[9] M.H. Dehghani, S. Nazmara, A. Zahedi, M. Rezanasab, E. Nikfar, V. Oskoei, Efficiency rate of photocatalytic UV/ZnO in removing humic acid from aqueous solution, J. Mazandaran. Univ. Med. Sci., 24 (2015) 264–277.

[10] I. Sutzkover-Gutman, D. Hasson, R. Semiat, Humic substances fouling in ultrafiltration processes, Desalination, 261 (2010) 218–231.

[11] R. Lamsal, M.E. Walsh, G.A. Gagnon, Comparison of advanced oxidation processes for the removal of natural organic matter, Water Res., 45 (2011) 3263–3269.

[12] C. Lu, F. Su, Adsorption of natural organic matter by carbon nanotubes, Sep. Purif. Technol., 58 (2007) 113–121.

[13] V. Gupta, O. Moradi, I. Tyagi, S. Agarwal, H. Sadegh, R. Shahryari-Ghoshekandi, A. Makhlouf, M. Goodarzi, A. Garshasbi, Study on the removal of heavy metal ions from industry waste by carbon nanotubes: effect of the surface modification: a review, Crit. Rev. Environ. Sci. Technol., 46 (2016) 93–118.

[14] C. Li, Y. Dong, D. Wu, L. Peng, H. Kong, Surfactant modified zeolite as adsorbent for removal of humic acid from water, Appl. Clay Sci., 52 (2011) 353–357.

[15] A.A.M. Daifullah, B.S. Girgis, H.M.H. Gad, A study of the factors affecting the removal of humic acid by activated carbon prepared from biomass material, Colloid Surf. A-Physicochem. Eng., 235 (2004) 1–10.

[16] T. Anirudhan, M. Ramachandran, Surfactant-modified bentonite as adsorbent for the removal of humic acid from wastewaters, Appl. Clay Sci., 35 (2007) 276–281.

[17] L. Wang, C. Han, M.N. Nadagouda, D.D. Dionysiou, An innovative zinc oxide-coated zeolite adsorbent for removal of humic acid, J. Hazard. Mater., 313 (2016) 283–290.

[18] X. Zhang, R. Bai, Mechanisms and kinetics of humic acid adsorption onto chitosan-coated granules, J. Colloid Interface Sci., 264 (2003) 30–38.

[19] M. Anbia, S. Khoshbooei, Functionalized magnetic MCM-48 nanoporous silica by cyanuric chloride for removal of chlorophenol and bromophenol from aqueous media, J. Nanostructure. Chem., 5 (2015) 139–146.

[20] T. Moriguchi, K. Yano, M. Tahara, K. Yaguchi, Metal-modified silica adsorbents for removal of humic substances in water, J. Colloid. Interface Sci., 283 (2005) 300–310.

[21] T. Hartono, S. Wang, Q. Ma, Z. Zhu, Layer structured graphite oxide as a novel adsorbent for humic acid removal from aqueous solution, J. Colloid. Interface Sci., 333 (2009) 114–119.

[22] K. Zare, V.K. Gupta, O. Moradi, A.S.H. Makhlouf, M. Sillanpää, M.N. Nadagouda, H. Sadegh, R. Shahryari-ghoshekandi, A. Pal, Z.-j. Wang, A comparative study on the basis of adsorption capacity between CNTs and activated carbon as adsorbents for removal of noxious synthetic dyes: a review, J. Nanostructure. Chem., 5 (2015) 227–236.

[23] H. Sadegh, G.A. Ali, V.K. Gupta, A.S.H. Makhlouf, R. Shahryari-ghoshekandi, M.N. Nadagouda, M. Sillanpää, E. Megiel, The role of nanomaterials as effective adsorbents and their applications in wastewater treatment, J. Nanostructure. Chem., (2017) 1–14.

[24] D. Robati, B. Mirza, M. Rajabi, O. Moradi, I. Tyagi, S. Agarwal, V. Gupta, Removal of hazardous dyes-BR 12 and methyl orange using graphene oxide as an adsorbent from aqueous phase, Chem. Eng. J., 284 (2016) 687–697.

[25] E.M. Elnaggar, K.I. Kabel, A.A. Farag, A.G. Al-Gamal, Comparative study on doping of polyaniline with graphene and multi-walled carbon nanotubes, J. Nanostructure. Chem., 7 (2017) 75–83.

[26] Y. Saghapour, M. Aghaie, K. Zare, Thermodynamic study of lead ion removal by adsorption onto nanographene sheets, J. Phys. Theor. Chem., 10 (2013) 59–67.

[27] K.S. Novoselov, Z. Jiang, Y. Zhang, S. Morozov, H.L. Stormer, U. Zeitler, J. Maan, G. Boebinger, P. Kim, A.K. Geim, Room-temperature quantum Hall effect in graphene, Science, 315 (2007) 1379–1379.

[28] J.P. Naik, P. Sutradhar, M. Saha, Molecular scale rapid synthesis of graphene quantum dots (GQDs), J. Nanostructure. Chem., 7 (2017) 85–89.

[29] J.-W. Jiang, B.-S. Wang, J.-S. Wang, H.S. Park, A review on the flexural mode of graphene: lattice dynamics, thermal conduction, thermal expansion, elasticity and nanomechanical resonance, J. Phys. Condens. Matter., 27 (2015) 083001.

[30] I. Shown, A. Ganguly, Non-covalent functionalization of CVD-grown graphene with Au nanoparticles for electrochemical sensing application, J. Nanostructure. Chem., 6 (2016) 281–288.

[31] C. Mattevi, H. Kim, M. Chhowalla, A review of chemical vapour deposition of graphene on copper, J. Mater. Chem., 21 (2011) 3324–3334.

[32] O.C. Compton, S.T. Nguyen, Graphene oxide, highly reduced graphene oxide, and graphene: versatile building blocks for carbon-based materials, Small, 6 (2010) 711–723.

[33] Q. Liu, J. Shi, J. Sun, T. Wang, L. Zeng, G. Jiang, Graphene and graphene oxide sheets supported on silica as versatile and high-performance adsorbents for solid-phase extraction, Angew. Chem.-Int., 123 (2011) 6035–6039.

[34] A. Azari, M. Salari, M.H. Dehghani, M. Alimohammadi, H. Ghaffari, K. Sharafi, N. Shariatifar, M. Baziar, Efficiency of magnitized graphene oxide nanoparticles in removal of 2,4-dichlorophenol from aqueous solution, J. Mazandaran. Univ. Med. Sci., 26 (2017) 265–281.

[35] A. Omri, M. Benzina, W. Trabelsi, N. Ammar, Adsorptive removal of humic acid on activated carbon prepared from almond shell: approach for the treatment of industrial phosphoric acid solution, Desal. Water Treat., 52 (2014) 2241–2252.

[36] X. Yang, C. Chen, J. Li, G. Zhao, X. Ren, X. Wang, Graphene oxide-iron oxide and reduced graphene oxide-iron oxide hybrid materials for the removal of organic and inorganic pollutants, RSC. Adv., 2 (2012) 8821–8826.

[37] A. Naghizadeh, Regeneration of carbon nanotubes exhausted with humic acid using electro-Fenton technology, Arab. J. Sci. Eng., 41 (2016) 155–161.

[38] A. Naghizadeh, F. Ghasemi, E. Derakhshani, H. Shahabi, Thermodynamic, kinetic and isotherm studies of sulfate removal from aqueous solutions by graphene and graphite nanoparticles, Desal. Water Treat., 80 (2017) 247–254.

[39] A. Naghizadeh, R. Nabizadeh, Removal of reactive blue 29 dye by adsorption on modified chitosan in the presence of hydrogen peroxide, Environ. Prot. Eng., 42 (2016).

[40] O. Moradi, K. Zare, Adsorption of Pb (II), Cd (II) and Cu (II) ions in aqueous solution on SWCNTs and SWCNT–COOH surfaces: kinetics studies, Fullerenes, Fuller. Nanotub. Carbon Nanostruct., 19 (2011) 628–652.

[41] A. Naghizadeh, S. Nasseri, A. Rashidi, R.R. Kalantary, R. Nabizadeh, A. Mahvi, Adsorption kinetics and thermodynamics of hydrophobic natural organic matter (NOM) removal from aqueous solution by multi-wall carbon nanotubes, Water Sci. Technol.-Water Supply, 13 (2013) 273–285.

[42] A. Naghizadeh, Comparison between activated carbon and multiwall carbon nanotubes in the removal of cadmium (II) and chromium (VI) from water solutions, J. Water Supply Res. Technol.-Aqua, 64 (2015) 64–73.

[43] L. Zhuravlev, The surface chemistry of amorphous silica. Zhuravlev model, Colloid Surf. A-Physicochem. Eng., 173 (2000) 1–38.

[44] S.-g. Wang, W.-x. Gong, X.-w. Liu, B.-y. Gao, Q.-y. Yue, D.-h. Zhang, Removal of Fulvic Acids from Aqueous Solutions via Surfactant Modified Zeolite11 Supported by the National High-tech and Development of Program of China (No. 2003AA601060), Chemical Research in Chinese Universities, 22 (2006) 566–570.

[45] A. Naghizadeh, F. Momeni, E. Derakhshani, Efficiency of ultrasonic process in regeneration of graphene nanoparticles saturated with humic acid, Desal. Water Treat., 70 (2017) 290–293.

[46] S. Gueu, B. Yao, K. Adouby, G. Ado, Kinetics and thermodynamics study of lead adsorption on to activated carbons from coconut and seed hull of the palm tree, Int. J. Environ. Sci. Technol., 4 (2007) 11–17.

[47] E. Errais, J. Duplay, F. Darragi, I. M'Rabet, A. Aubert, F. Huber, G. Morvan, Efficient anionic dye adsorption on natural untreated clay: Kinetic study and thermodynamic parameters, Desalination, 275 (2011) 74–81.

[48] Z. Zhu, H. Zeng, Y. Zhu, F. Yang, H. Zhu, H. Qin, W. Wei, Kinetics and thermodynamic study of phosphate adsorption on the porous biomorph-genetic composite of α-$Fe_2O_3/Fe_3O_4/C$ with eucalyptus wood microstructure, Sep. Purif. Technol., 117 (2013) 124–130.

[49] M. Yari, M. Norouzi, A.H. Mahvi, M. Rajabi, A. Yari, O. Moradi, I. Tyagi, V.K. Gupta, Removal of Pb (II) ion from aqueous solution by graphene oxide and functionalized graphene oxide-thiol: effect of cysteamine concentration on the bonding constant, Desal. Water Treat., 57 (2016) 11195–11210.

[50] C. Dong, W. Chen, C. Liu, Preparation of novel magnetic chitosan nanoparticle and its application for removal of humic acid from aqueous solution, Appl. Surf. Sci., 292 (2014) 1067–1076.

[51] W.W. Ngah, M. Hanafiah, S. Yong, Adsorption of humic acid from aqueous solutions on crosslinked chitosan–epichlorohydrin beads: kinetics and isotherm studies, Colloid Surf. B-Biointerfaces, 65 (2008) 18–24.